

A phenomenological model for the pressure sensitivity of the Curie temperature in hole-doped manganites

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We performed high pressure experiments on $\text{La}_{0.8}\text{Ca}_{0.2-x}\text{Sr}_x\text{MnO}_3$ (LCSMO) ($0 \leq x \leq 0.2$) ceramic samples in order to analyze the validity of the well known relation between the A mean ionic radius ($\langle r_A \rangle$) and the Curie temperature T_c of hole-doped manganites at a fixed doping level and for doping values below the 0.3 ($\text{Mn}^{+4}/\text{Mn}^{+3}$) ratio. By considering our results and collecting others from the literature, we were able to propose a phenomenological law that considers the systematic dependence of T_c with structural and electronic parameters. This law predicts fairly well the pressure sensitivity of T_c , its dependence with the A-cation radius disorder and its evolution in the high pressure range. Considering a Double Exchange model, modified by polaronic effects, the phenomenological law obtained for T_c can be associated with the product of two terms: the polaronic modified bandwidth and an effective hole doping.

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I. INTRODUCTION

Many efforts have been devoted to determine the relevant electronic and structural parameters that fix the Curie temperature (T_c) of manganites^{1,2,3}. The Double Exchange model^{4,5} (DE) was initially applied in order to correlate electrical transport properties and magnetic ordering in these compounds. But early experiments such as the temperature dependence of the Hall coefficient⁶, the differences in the activation energy between thermopower and conductivity⁷, and the isotope effect⁸ demonstrated the polaronic nature of the carriers. This evidence showed the necessity for introducing polaronic corrections to the electronic bandwidth that determines T_c .

On the other hand, it was experimentally established that, for hole-doped manganites and particularly for the family $\text{A}'_{0.7}\text{A}''_{0.3}\text{MnO}_3$ (where A' is a trivalent rare earth ion and A'' a divalent alkali earth ion), the resulting A mean ionic radius ($\langle r_A \rangle$) has a clear influence on T_c .⁹ Experiments also showed that $\langle r_A \rangle$ can be varied both by chemical replacement or by an external pressure⁹, where in the former case, both the Mn-O bond distance and the Mn-O-Mn bond angle vary while in the latter case, most of the variation comes from the Mn-O bond distance.² Although the $T_c(\langle r_A \rangle)$ dependence can be well reproduced by varying the pressure just by considering a linear dependence $\delta\langle r_A \rangle = \gamma\delta P$ ($\gamma = 3.75 \cdot 10^{-4} \text{ \AA/kbar}$) for $P \leq 20$ kbar. In this low pressure range, T_c varies linearly with P , while for higher pressures, T_c reaches a maximum value and decreases for a further increase of P .^{10,11} This behavior seems to be related to pressure-dependent competing interactions, like the ferromagnetic (F) and the antiferromagnetic (AF) coupling between the core spins, as suggested by Sacchetti et al.¹³, although other factors that govern the polaronic modified DE model can play a major role. On the other hand, Rivadulla et al.¹²

made a good quantitative description of the $\langle r_A \rangle$ dependence of T_c at constant doping based on a mean field model where the reduction of the volume fraction of the itinerant electrons produced by the phase separation is responsible for the observed behavior.

Empirically, the temperature dependence of the pressure (P) sensitivity of T_c ($d\ln T_c/dP$) was established, which seems to represent a universal behavior for many moderated hole-doped manganites¹⁴. This curve could be described qualitatively within the small polaron modified DE model but it was far from quantitative¹⁵ and even considering polarons in the more suitable intermediate electron-phonon coupling regime did not produce a better understanding.¹⁶

In this paper we present a phenomenological model based on the $\langle r_A \rangle$ dependence of T_c for intermediate to large bandwidth AMnO_3 hole-doped perovskites which usefully describes the quantitative dependence of $T_c(P)$. A DE interaction, modified by polaronic effects and also an effective doping of the MnO planes, both controlled by $\langle r_A \rangle$ are suggested as the two microscopic ingredients that govern the proposed relation.

II. EXPERIMENTAL

Previous experiments⁹ showed that T_c follows a parabolic dependence with $\langle r_A \rangle$ for $\text{La}_{1-y}\text{T}_y\text{MnO}_3$ ($\text{T}=\text{Sr}; \text{Ca}; \text{Pr}$) for a fixed doping level $y \sim 0.3$. Here, in order to test the validity of this dependence for other doping levels ($y = 0.2$), we performed resistivity measurements as a function of temperature and pressure on $\text{La}_{0.8}\text{Ca}_{0.2-x}\text{Sr}_x\text{MnO}_3$ (LCSMO) ($0 \leq x \leq 0.2$) ceramic samples. These samples were synthesized following a similar process to the one published elsewhere.¹⁷ The temperature dependence of resistivity was measured using a conventional 4 terminal DC technique in a CuBe

piston-cylinder hydrostatic cell described previously.¹⁸ Pressures up to 10 kbar were applied using a 50 % mixture of kerosene and transformer oil as the pressure transmitting medium. Pressure was measured at room temperature by using a calibrated InSb sensor and it remains constant over all the temperature range (within a 10% of variation for a temperature span of 77 K to 350 K) in spite of thermal contractions. Temperature was measured using a calibrated carbon-glass thermometer in good thermal contact with the cell's body.

III. RESULTS AND DISCUSSION

The normalized resistivity as a function of temperature of the LCSMO series with $0 \leq x \leq 0.2$ and $y=0.2$ can be observed in Fig. 1. All the curves show a change in the conduction regime that can be associated with a metal to insulator transition (T_{MI}), which increases with increasing Sr content.

The pressure sensitivity of the resistivity is shown in Fig. 2 for samples LCSMO with $x=0$; 0.06 and 0.20. Pressure increases both T_{MI} and the conductivity of these materials.

T_{MI} does not necessarily coincide with the Curie temperature, so we determine T_c from the resistivity curves as the temperature at which a sudden increase in the logarithmic temperature derivative of the resistivity is observed. It has been shown previously that this coincides with the T_c determined by magnetization measurements.¹⁹ By following this criteria and by calculating the variation on $\langle r_A \rangle$ generated by chemical replacements (from Shannons tables of ionic radii²⁰) or by external pressure (assuming that γ is independent of the doping level and that $\langle r_A \rangle$ is the only pressure-dependent parameter), we obtain the dependence of T_c as a function of $\langle r_A \rangle$ for the LCSMO ($y = 0.2$) samples, shown in Fig. 3.

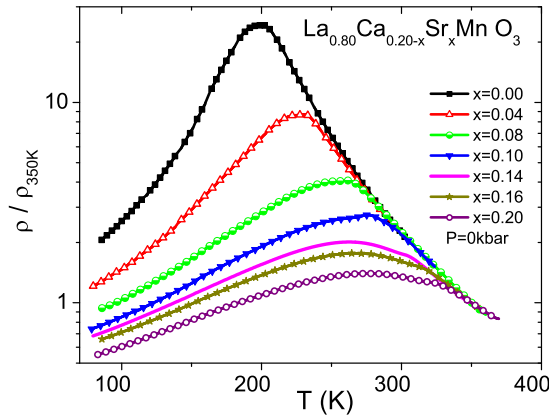


FIG. 1: (Color online) Temperature dependence of the normalized resistivity of $\text{La}_{0.8}\text{Ca}_{0.2-x}\text{Sr}_x\text{MnO}_3$ ($0 \leq x \leq 0.2$)

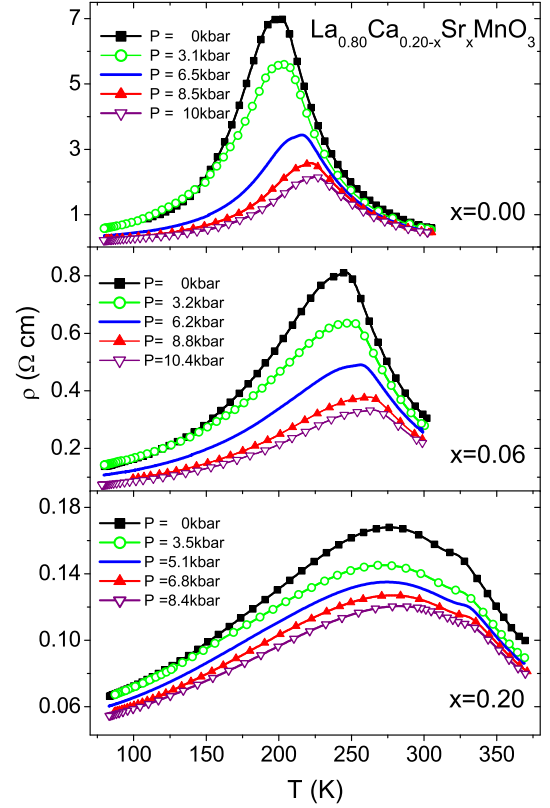


FIG. 2: (Color online) Pressure sensitivity of the resistivity as a function of temperature of $\text{La}_{0.8}\text{Ca}_{0.2-x}\text{Sr}_x\text{MnO}_3$ ($x=0$; 0.06; 0.2).

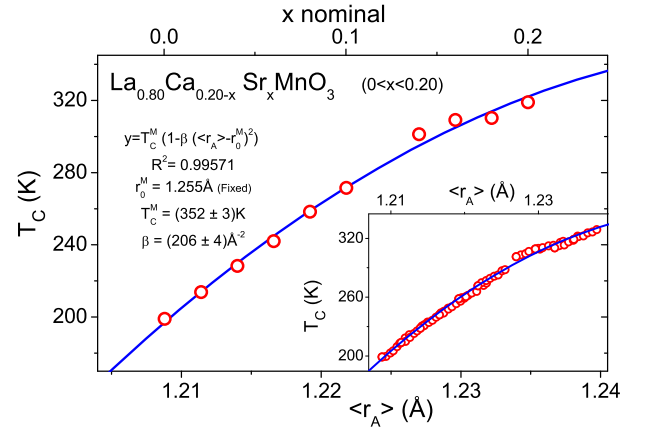


FIG. 3: (Color online) T_c vs the Sr concentration (x) or the average ionic radius of the cation in the A site ($\langle r_A \rangle$) at constant doping $y = 0.2$. The line is a fit using Eq. 1; the fitting parameters are displayed. The inset also shows T_c vs $\langle r_A \rangle$, but where the variation of $\langle r_A \rangle$ is due to both chemical replacements and external pressure (assuming that $\delta T_c^M / dP = \delta \beta / dP = 0$ and $\delta \langle r_A \rangle = \gamma \delta P$, with $\gamma = 3.75 \cdot 10^{-4} \text{ Å/kbar}$).

The data is very well represented by a quadratic law for the whole pressure and doping intervals considered, which indicates that the assumptions we made were quite reasonable. A small departure from the ideal dependence can be observed for $\langle r_A \rangle \simeq 1.227$ Å, which coincides with a structural transition reported for this series.²¹

From our data and the data already published we can extend the study of the $T_c(\langle r_A \rangle)$ dependence for other manganites and for doping levels y in the $0.15 \leq y \leq 0.33$ range. The obtained $T_c(y, \langle r_A \rangle)$ curves, shown in Fig. 4, follow the same general behavior: a parabolic law for each doping concentration and a doping-dependent maximum $[T_c^M(y)]$ located at $\langle r_A^M \rangle \simeq 1.255$ Å. This dependence can be represented by an expression of the form

$$T_c(y, \langle r_A \rangle) = T_c^M(y) \left[1 - \beta(y) (\langle r_A \rangle(x, y) - \langle r_A^M \rangle)^2 \right], \quad (1)$$

By fitting the data presented in Fig. 4 we can determine the doping sensitivity of parameters T_c^M and β , as can be observed in Fig. 5. As was shown in a previous study²⁶, the local structural disorder, generated by the occupation of the A site by cations with different sizes, produces a reduction of the ideal T_c that would be measured in case that this disorder does not exist. The disorder can be quantified by the variance σ^2 of the A -cation radius distribution. In order to perform the fits, minimizing in this way the contribution of disorder in the obtained parameters, we choose from the $T_c(y, \langle r_A \rangle, \sigma)$ data the points with small σ^2 ($< 10^{-3}$ Å²). On the other hand, if we assume that Eq. 1 gives the T_c of a manganite with negligible A -cation radius disorder

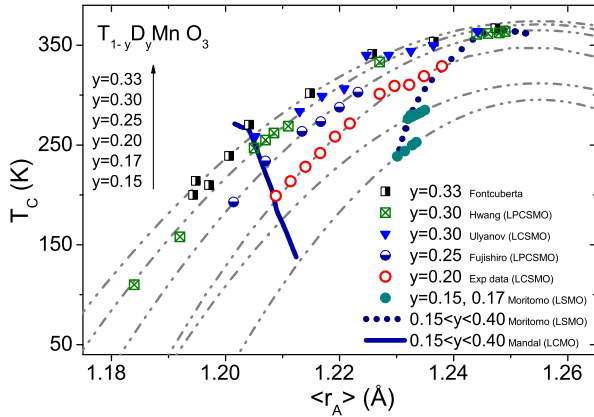


FIG. 4: (Color online) The phase diagram of $T_{1-y}D_yMnO_3$ (where T is a trivalent lanthanide as La, Sm, Nd, and D a divalent alkaline earth as Ca, Sr) for $0.15 \leq y \leq 0.33$ as a function of $\langle r_A \rangle$. Data was extracted from references^{9,21,22,23,24,25}. The dashed lines are parabolic fits corresponding to Eq. 1 at constant doping y . The evolution of T_c and $\langle r_A \rangle$ is also shown for the Sr and Ca-doped LMO samples (i.e. samples with a varying y).

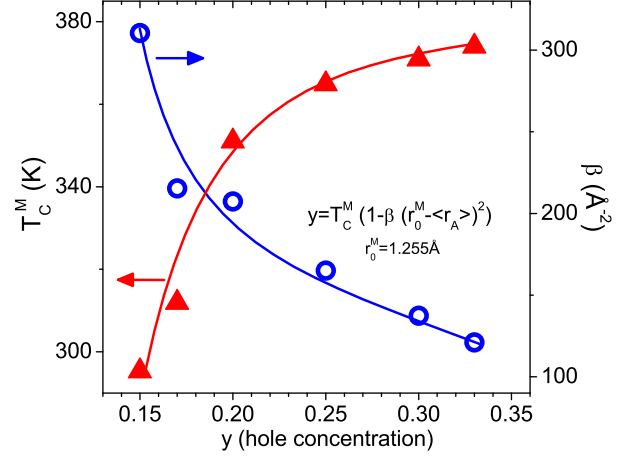


FIG. 5: (Color online) The fitted parameters T_c^M and β as a function of the hole concentration y . Lines are guides to the eye.

$[T_c^*(x, \langle r_A \rangle) = T_c(x, \langle r_A \rangle, \sigma = 0)]$, we can estimate the T_c of a manganite with a structural disorder σ in r_A as the mean T_c resulting from a uniform distribution of cells with A -cation radii within the interval $r_A \pm \sigma$. The result gives an expression of the form

$$\langle T_c[y, \langle r_A \rangle, \sigma^2] \rangle = T_c^*(y, \langle r_A \rangle) - (T_c^M(y)\beta(y)/3)\sigma^2, \quad (2)$$

which gives a simple explanation of the linear dependence of T_c on σ^2 already published for the perovskite family $A_{0.7}A'_{0.3}MnO_3$.²⁶ The σ^2 's pre-factor can be calculated from the fitted parameters shown in Fig. 5. For $y = 0.3$ we obtain a value of (17.000 ± 1000) KÅ⁻², quite similar to the experimental data published. Also, we can qualitatively estimate the influence of the disorder on the pressure sensitivity of T_c by taking the pressure derivative of Eq. 2. If we compare the data of previous papers^{11,27} it is clear that $d\sigma^2/dP$ is an increasing function of σ , the second term of the right part of the derived equation would indicate a reduction of the expected pressure sensitivity of manganite with increasing σ^2 , as was experimentally obtained previously.²⁸ Besides, considering the similarity of Eq. (1) with the one developed by Bean and Rodbell²⁹ to describe the coupling of magnetic order to structural distortions, a first order magnetic phase transition at T_c can be predicted for large values of β , as was demonstrated experimentally by Otero-Leal et al..²⁸

The expression of the pressure sensitivity of T_c , shown in Eq. 3, can be easily obtained from Eq. 1 as,

$$\frac{d \ln T_c}{dP} = \frac{d \ln T_c^M}{dP} + 2\gamma\sqrt{\beta} \sqrt{\frac{T_c^M}{T_c} \left(\frac{T_c^M}{T_c} - 1 \right)}, \quad (3)$$

By using Eq. 3 and the fitted parameters $T_c^M(y)$ and $\beta(y)$, the pressure sensitivity of T_c at low pressures can

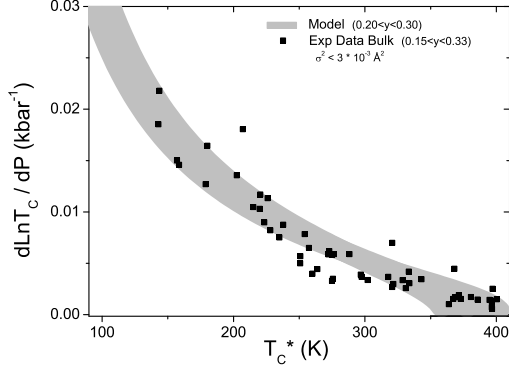


FIG. 6: Pressure sensitivity as a function of T_c^* for compounds of the $\text{La}_{1-y}\text{T}_y\text{MnO}_3$ family ($\text{T}=\text{Sr}; \text{Ca}; \text{Y}, \text{Dy}$) in the $0.15 \leq y \leq 0.33$ range. To guarantee the range of validity of Eq. 2 in order to estimate T_c^* , data points with $\sigma < 3 \cdot 10^{-3} \text{ \AA}^2$ were extracted from references^{9,10,11,15,16,21,22,24,30,31} and from our measurements. The shaded area represents the predictions of the model (Eq.3) taking into account the different values of the fitted parameters (β and T_c^M).

be predicted for many compounds. A good accordance between experimental points and the predicted behavior, represented by a shaded area as we considered the doping dependence of the fitted parameters, can be observed in Fig. 6. Here, we included data points where T_c was determined by different criteria and techniques (ac susceptibility or resistivity) which accounts for the dispersion of data. We only applied the restriction that the selected data points should be derived from compounds with a small structural disorder in r_A ($\sigma < 3 \cdot 10^{-2} \text{ \AA}$). Although some of the pressure sensitivities seem to be overestimated, the general behavior is very well predicted as a direct consequence of the validity of Eq. 1 and the linear dependence of $\langle r_A \rangle$ to describe the general behavior of intermediate to large bandwidth manganites in the low pressure range considered here ($P < 1 \text{ GPa}$). For higher pressures, the linear dependence of $\langle r_A \rangle$ with pressure is no longer valid, considering the asymptotic behavior of the structural parameters¹¹. This fact also explains why our model predicts a parabolic evolution of T_c with pressure, while the experimental result in the high pressure range ($P > 6 \text{ GPa}$) reveals an asymptotic behavior³⁰.

Additionally, in this pressure range, pressure induces distortions in the MnO_6 octahedra¹¹ that can produce a departure from the expected ideal behavior described by our empirical model. Finally, we would like to gain insight on the physical origin of each term in Eq. 1. As $T_c \sim W n$, where W is the bandwidth and n is related to the electronic density³², we may associate T_c^M with W , and the expression between brackets with n , that, more precisely, may represent the relative variation with $\langle r_A \rangle$

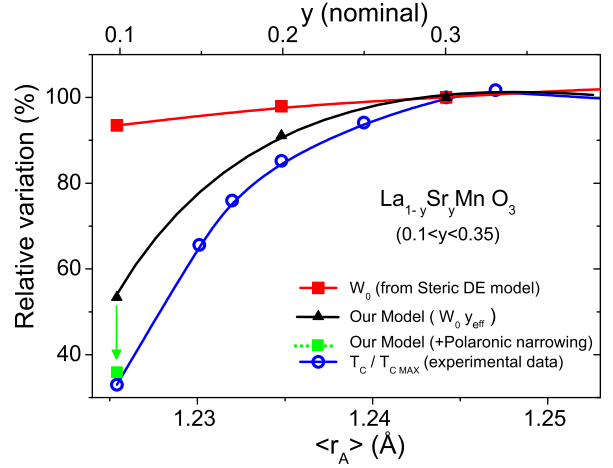


FIG. 7: (Color online) The relative variation of the bare bandwidth W_0 , of W_0 times the term in brackets of Eq. 1, of the polaronic correction in the intermediate to strong coupling regime and of the experimental T_c (from reference²⁴), as a function of the nominal doping y or of $\langle r_A \rangle$. The arrow shows the correction added by polaronic effects (only valid for low doping levels).

of an effective density of carriers. One possible association of this n can be established with the n at $T \sim T_c$ estimated from thermal expansion experiments by Rivadulla et al.¹² ($n = 1 - n_{JT}$, where n_{JT} is the volume fraction of electrons in the polaronic phase) used to determine the $T_c[\langle r_A \rangle(x)]$ dependence at constant doping for the system $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$. This implies that, not only the steric factors that govern the hopping energy and the polaronic coupling constant that modify the bandwidth will affect the T_c of the manganite by changing T_c^M , but also, and quantitatively more important, variations on $\langle r_A \rangle$ will determine its value by modifying the effective value of n . In this way, we may associate T_c^M with structural parameters and with the polaronic narrowing of the bandwidth as³³

$$T_c^M \sim W_0 F(E_b) = \frac{\cos(w)}{d^{3.5}} F(E_b), \quad (4)$$

where W_0 is the bare bandwidth, w is the tilt angle in the plane of the Mn-O bond, d the Mn-O bond length, E_b the binding energy of polarons and F the appropriate function that accounts for the polaronic bandwidth reduction.

In Fig. 7 we have plotted the relative variation of the experimental T_c with $\langle r_A \rangle$ for samples of the LSMO family. In the same figure we considered the relative variation of W_0 , based on the modification of the steric factors. Again, it is clear that the DE model is far to explain the experimental variation of T_c . If we include the correction of the effective doping proposed in our phenomenological model a much better agreement is obtained ($W_0 y_{eff}$).

Finally, if we use the expression $F(E_b) = \exp(\frac{\gamma E_b}{\hbar\omega})$, only valid for low doping levels as, in this range, we are near the frontier from strong to intermediate electron-phonon coupling^{34,35}, we can additionally estimate the polaronic bandwidth reduction of W_0 by using the appropriate constants³⁶. The excellent agreement with the measured data obtained (marked with an arrow in Fig. 7) indicates that the association of T_c^M with W is a reliable assumption.

IV. CONCLUSIONS

An empirical law that determines the T_c of $T_{1-y}D_yMnO_3$ compounds as a function of $\langle r_A \rangle$ and the doping level y was experimentally extended, using our data and data already published in the literature for dopings in the $0.15 \leq y \leq 0.33$ range. For these compounds

and in the pressure range where a linear dependence of $\langle r_A \rangle$ with pressure is still valid, the influence of cationic disorder and the pressure sensitivity of T_c was quantitatively described by an empirical relation that associates T_c with the polaronic modified bandwidth and with an effective doping level, controlled by $\langle r_A \rangle$.

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